

INFLUENCE OF MACERAL COMPOSITION OF RAW COAL ON
POTASSIUM ACTIVITY IN STEAM GASIFICATION OF CHARs

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INTRODUCTION

The catalytic effect of potassium salts on steam gasification rate of coal chars, is one of the subjects in the field of coal gasification most widely investigated because of their potential application in commercial processes. The results of research activity, have pointed out that the catalytic activity of potassium depends upon several factors such as associated ion, mineral matter, rank of parent coal, pretreatment conditions and K/C ratio[1]. As regards the latter, literature data show that gasification rates increase with potassium content until a particular value is reached after which higher values are ineffective or lead to a decrease in reactivity [2]. Moreover, it has been reported that the value of catalyst concentration at which the gasification rate saturates depends on the identity of the substrate and the procedure used to prepare the doped char[3]. The objective of the work reported here was to investigate the influence of maceral composition of the parent coal on the catalytic behavior of potassium carbonate in steam gasification of chars.

EXPERIMENTAL

Four coals were used in this study: three bituminous coals (Illinois N°6, Middelburg (S.A), Polish) and a subbituminous Sulcis coal. Table 1 shows their maceral composition and the respective rank determined by petrographic analysis. In all cases K_2CO_3 was added to the coals by mechanical mixing before pyrolysis. A known amount of powdered catalyst was added to the coal (150 - 300 μm), homogenized and then charified at 1073 °K for 2 h under nitrogen

flow. After pyrolysis the doped chars were ground, sieved and the fraction 150-300 μm was used for this study. Potassium loading on chars was determined by AES-ICP technique on the solution obtained after an oxidizing treatment with $\text{HNO}_3\text{-H}_2\text{O}_2$ solution of doped samples. The kinetic experiments were carried out under a steam pressure of 3,6 MPa using a small bench-scale apparatus with a semicontinuous fixed-bed reactor consisting of 0.0127 m i.d., 0.7m long stainless steel pipe, water precision pump and steam preheater. After loading the reactor with the doped char the temperature was raised (flowing N_2) to the desired value and then the sample was reacted stopping the nitrogen flow and pumping water. The reaction temperature was 1018 °K for chars obtained from Polish coal and 973 °K for those from Illinois N°6, Sulcis, and Middleburg coals. After water removal, the product gas was sampled and analyzed by a gaschromatograph. Reactivity during gasification was determined by measuring the reaction rate ($\text{mol} \cdot \text{h}^{-1}$) normalized with respect to the initial moles of carbon in the sample.

RESULTS AND DISCUSSION

The catalytic activity of K_2CO_3 towards steam gasification of the coal chars with different catalyst concentration was evaluated determining the reaction rate at 50% conversion. The relationships between reactivity and K/C ratio, shown in figure 1, point out a different trend for the chars examined. Leaving out the first part of the curves whose lower slopes are mainly due to the reaction of potassium with mineral matter[4], chars from Sulcis and Illinois N°6 coals display a linear correlation in the whole range of catalyst concentration. Differently, in the case of chars from Middleburg and Polish coals the concentration of active sites increases linearly with catalyst concentration up to a limit value after which further addition of catalyst is less effective. Studies carried out by several investigators using different substrates have yielded some conflicting results. For example Wigmans et al.[5] reported a linear increase of reactivity with catalyst loading up to 40%w. In contrast other authors [6,7] have found that gasification rates saturate at much lower K/C ratios. Generally the variation of saturation limit has been explained in terms of different preparation methods used to load the catalyst, potassium

volatilization or micropore blockage by catalyst [2,3,6,7]. In our case the preparation method was always the same and no loss of potassium was detected during gasification experiments. All this strongly suggests that besides the above mentioned factors, the value of K/C ratio at which the catalyst begins to be less effective should be also dependent on the particular features of the substrate and the interactions between catalyst and coal during the pyrolysis step. The results of petrographic analyses of the coals used in this study, listed in table 1, point out that the vitrinite content in Illinois N°6 and Sulcis coals is remarkably higher than in Polish and Middelburg coals. In this connection it is interesting to note that the decrease of catalytic activity of potassium after a given value of K/C ratio occurs only with the chars obtained from the two coals having the lowest vitrinite content. During the pyrolysis process (with or without catalyst) vitrinite undergoes to substantial changes of its chemical composition, porous structure and morphology which leads to the development of macroporosity whereas the inertinite remains almost unchanged. This situation is illustrated in figures 2, 3, 4 and 5 which show vitrinite and inertinite fragments before and after pyrolysis. It is known that upon heating the catalyst becomes extremely mobile and spreads over the accessible carbon surface through the porous system [8]. On this ground, it follows that the porosity originated during the pyrolysis step promotes the contact between catalyst and the "support" and the distribution of potassium in the char matrix. An example is given in figure 6 where the oblique section of a vitrinite fragment shows how the pores can be easily penetrated by the catalyst during pyrolysis. On the contrary inertinite fragments do not develop macroporosity upon heating (fig. 7) and therefore it is reasonable to expect that higher contents of this maceral could lead to a lower ability of the coal to allow a constant dispersion of increasing quantity of catalyst. The examination of doped char samples by electron microscopy and microanalysis (SEM+EDS) confirms the hypothesis reported above. Indeed figures 8 and 9 show that the distribution of potassium on the surface of chars obtained from Polish coal is uneven and regions with higher potassium concentration are mainly those formed by pyrolysis of vitrinite. All this is particularly clear in figure 8 which shows a pyrolyzed inertinite fragment free

of potassium close to a "vitrinite" fragment with a high concentration of catalyst.

Conclusions

It has been demonstrated that regions of enhanced reaction rate are those associated with the interface between the "support" and added catalyst [9], therefore from a general point of view the existence of a linear relationship between reaction rate and K/C ratio implies a constant dispersion degree of the catalyst. In our case the porous system of the char through which the catalyst is dispersed is mainly the result of changes undergone by the vitrinite and its interaction with K_2CO_3 during the pyrolysis step. Hence the ability of a given char to allow a constant dispersion degree of increasing quantity of catalyst, besides the feature of the porous system and its evolution during gasification, will be also affected by the vitrinite content of the parent coal.

References

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Table 1. Maceral analyses of coals^(*)

Coal	Vitrin.	Inert.	Liptin.	Reflect. %	Rank
Sulcis	93	1	6	0.49	Subbitum.
Illinois N°6	94	3	3	0.58	HVB-C
Polish	53	38	9	0.92	HVB-A
Middelburg	48	46	6	0.64	HVB-C

(*) Data are given on mineral matter free basis (% volume).
 Reflectance percentages refer to vitrinite macerals
 HVB: High volatile bituminous

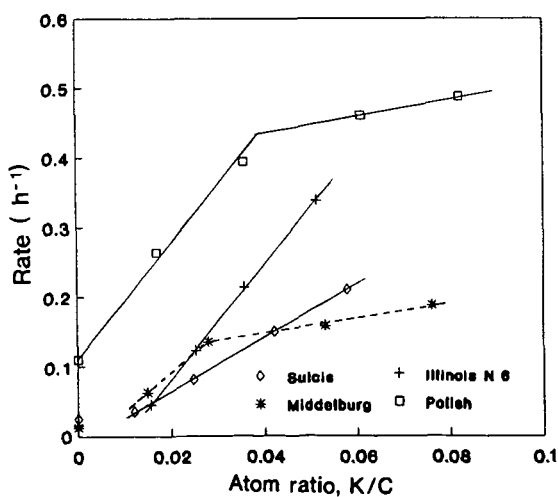


FIGURE 1. CATALYTIC EFFECT OF K_2CO_3 ON GASIFICATION RATES

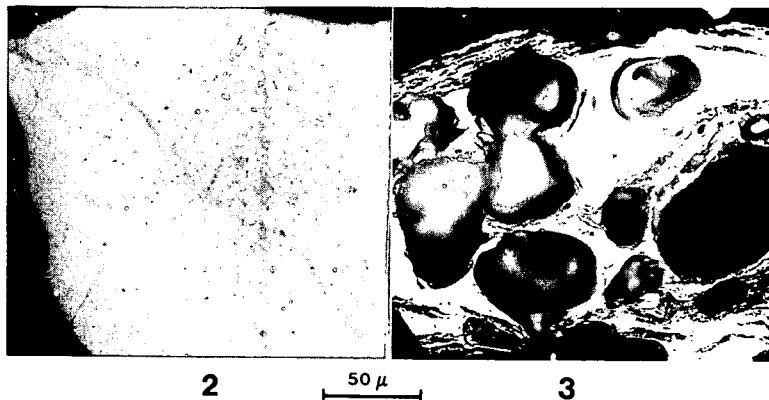


FIGURE 2 FRAGMENT OF VITRINITE IN RAW COAL

FIGURE 3 FRAGMENT OF PYROLYZED VITRINITE

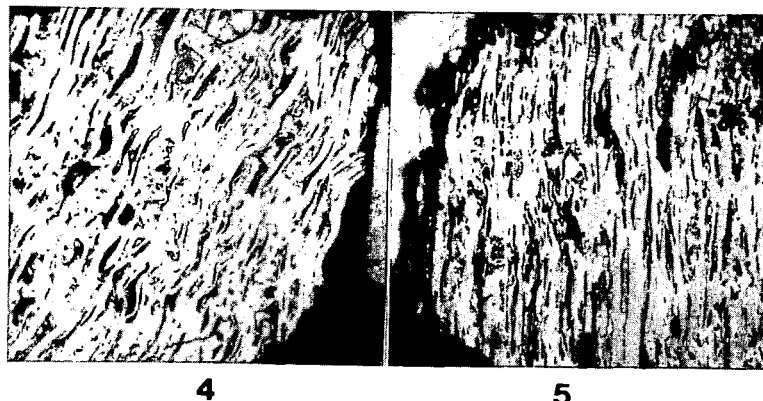


FIGURE 4 FRAGMENT OF FUSINITE (INERTINITE) IN RAW COAL

FIGURE 5 FRAGMENT OF PYROLYZED FUSINITE (INERTINITE)

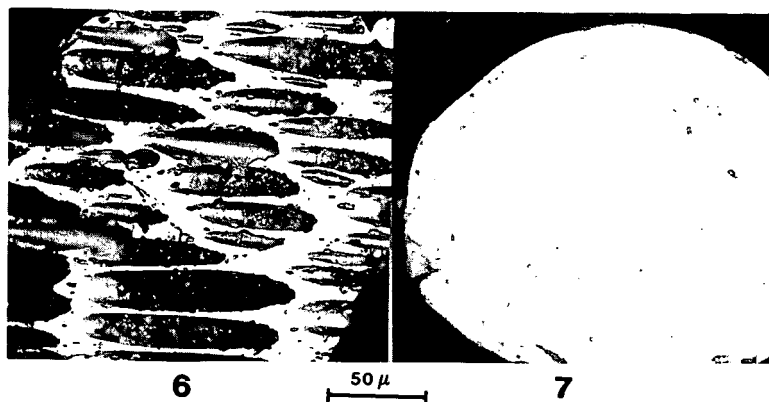


FIGURE 6 FRAGMENT OF PYROLYZED VITRINITE

FIGURE 7 FRAGMENT OF PYROLYZED MACRINITE

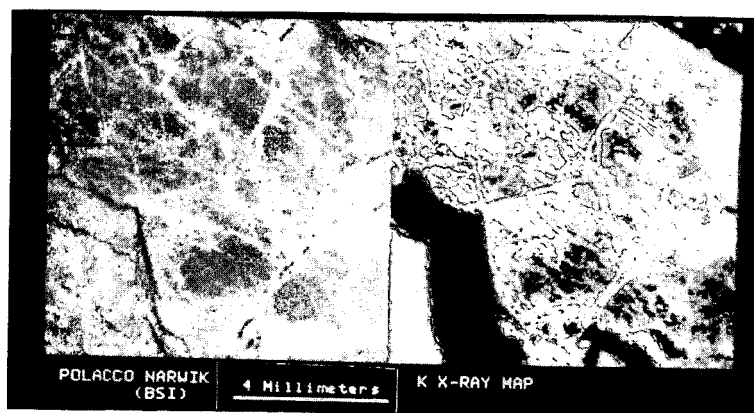


FIGURE 8. POTASSIUM DISTRIBUTION MAP OF DOPED POLISH CHAR

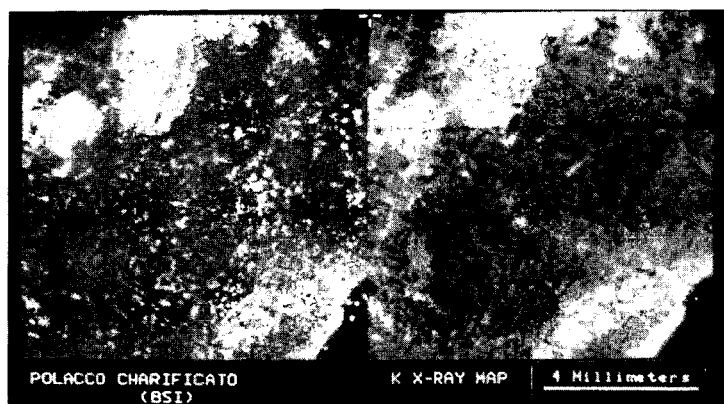


FIGURE 9. POTASSIUM DISTRIBUTION MAP OF DOPED POLISH CHAR